

Ab initio calculations on electronic states of CaOH

Giannoula Theodorakopoulos and Ioannis D. Petsalakis

Theoretical and Physical Chemistry Institute, The National Hellenic Research Foundation,
48 Vassileos Constantinou Ave., Athens 116 35 Greece

Heinz-Peter Liebermann and Robert J. Buenker

Bergische Universitaet Wuppertal, Fachbereich 9, Theoretische Chemie, Gausstrasse 20,
D-42097 Wuppertal, Germany

Jacek Koput

Department of Chemistry, Adam Mickiewicz University, Poznan, Poland

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Ab initio configuration interaction calculations have been carried out on the potential energy surfaces of the ground and the doublet excited electronic states of CaOH. The calculated transition energies are in good agreement with previous theoretical values and with the available experimental data. The calculated Ca–O stretching potentials at different values of the bond angle show typical Rydberg minima at short internuclear distances but are complicated for large $R_{\text{Ca-O}}$. The calculated bending potentials are rather shallow for deviations of 5° – 10° from linearity and, depending on the values of the Ca–O and O–H bond lengths, off-linear geometries have low energies. There is no evidence for the existence of an electronic state with bent equilibrium geometry, which would correspond to the reported state correlating with $\tilde{F}^2\Pi$ of CaOH. The $7^2A'$ state (which does correlate with $\tilde{F}^2\Pi$) is found to be quasi-linear with a barrier to linearity of only 92 cm^{-1} , and similarly the $4^2A''$ state (correlating with $\tilde{C}^2\Delta$) is found to be quasilinear with a barrier to linearity of 84 cm^{-1} . © 2002 American Institute of Physics. [DOI: 10.1063/1.1497680]

INTRODUCTION

Many experimental studies have been devoted during the past two decades to the spectroscopy of CaOH,¹ including millimeter wave rotational spectroscopy^{2,3} as well as studies of electronic transitions involving the $\tilde{A}^2\Pi$, $\tilde{B}^2\Sigma^+$, $\tilde{C}^2\Delta$, $\tilde{D}^2\Sigma^+$, $\tilde{E}^2\Sigma^+$, $\tilde{F}^2\Pi$, and $\tilde{G}^2\Pi$ states.^{4–10} The monohydroxide molecules of metals are of interest for studies of the chemistry of metallic elements in the envelopes of oxygen-rich stars as well as in molecular clouds.² It is predicted that CaOH is the most abundant molecule containing Ca at $T\sim 1000$ – 2000 K , although attempts to detect it have failed.^{2,11} Theoretical calculations on CaOH have been devoted to the ground state geometry and dissociation energy,^{12,13} to the equilibrium geometry and dipole moment of the lowest three electronic states,¹¹ to the determination of the different stable ground state geometries¹⁴ and also to the vertical transition energies at the ground state experimental geometry.^{15,16} The electronic structure of CaOH can be described by an ionic model, Ca^+OH^- , whereby the excited states are obtained by excitation of an unpaired Ca $4s$ electron into higher ns , np , and nd levels.^{9,11} Accordingly, the ground and these Rydberg excited states have similar (linear) geometry, which is consistent with theoretical work¹¹ and experimental findings for most of the observed excited states. A bent excited state has been proposed correlating with the $(3d)\tilde{F}^2\Pi$ linear state, as deduced from extensive activity in the bending vibration in the observed spectra,⁸ indicating considerable covalent character for this state. Configuration interaction calculations on the lighter members of this series,

BeOH and MgOH, where covalent bonding is expected to contribute, did find the first excited state, $2^2A'$, correlating with the $A^2\Pi$ of linear geometry, to have a bent equilibrium geometry in both systems.¹⁷ The $2^2A'$ state of BeOH was found to have a minimum energy geometry with a bond angle of 116° and a barrier to linearity of 3710 cm^{-1} , while the corresponding state of MgOH was found to have a minimum at 115° at a transition energy of 3.34 eV with respect to the ground state and with a barrier to linearity of 2216 cm^{-1} .¹⁷ These results are in good agreement with the existing experimental data for MgOH, with 119° for the bond angle, a transition energy of 3.299 eV and a barrier height of 1970 cm^{-1} .¹⁸ For the heavier system, SrOH, for which a number of transitions have been observed, linear geometries have been proposed for all the excited electronic states, including the $\tilde{C}^2\Pi$ state, in which substantial Renner–Teller activity is assumed, causing pronounced activity in the bending vibrational mode.¹⁹ Theoretical calculations of the potential energy curves of the excited states of CaOH which might clarify whether a bent excited state of this system exists have not yet been reported.

In the present work, *ab initio* multireference double excitations configuration interaction (MRD–CI) calculations^{20–22} on the doublet excited states of CaOH for linear and bent geometries are presented, in an effort to provide theoretical information for the spectroscopically observed states of this system. The present work is continuing the effort¹⁷ to determine structural trends for the metal monohydroxides and M–OH bond formation.

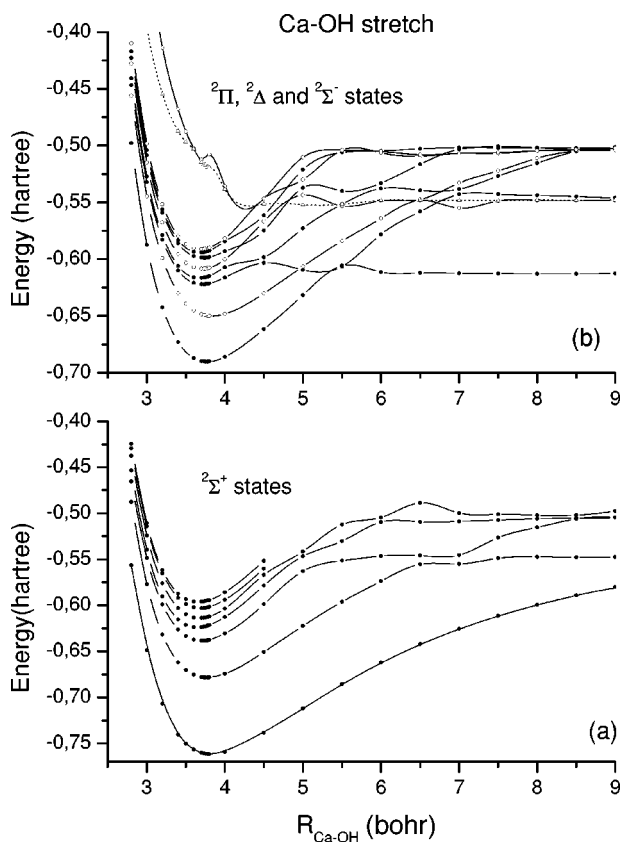
TABLE I. Valence atomic orbital basis sets^a employed in the present calculations for Ca and O.

| s-type exponent | p-type exponent | d-type exponent | f-type exponent |
|-----------------|------------------------|--------------------|-----------------|
| Ca | | | |
| 9.862 21 | 4.902 73 | 15.21 ^b | 1.4 |
| 3.977 75 | 1.921 43 | 4.08 ^b | 0.3 |
| 0.977 055 | 0.784 693 ^c | 1.32 | |
| 0.396 147 | 0.308 996 ^c | 0.454 | |
| 0.065 938 | 0.1522 | 0.1498 | |
| 0.026 902 | 0.074 979 | 0.044 | |
| 0.01 | 0.026 927 | 0.013 | |
| 0.004 | 0.01 | 0.003 | |
| | 0.004 | | |
| O | | | |
| 8.519 | 8.519 | 1.0 | |
| 2.073 | 2.073 | 0.3 | |
| 0.6471 | 0.6471 | | |
| 0.2 | 0.2 | | |
| | 0.059 | | |

^aAll uncontracted unless otherwise indicated.^bContraction coefficients 0.034 95 and 0.170 50 for upper and lower functions, respectively.^cContraction coefficients 0.5716 and 0.3282 for upper and lower functions, respectively.

CALCULATIONS

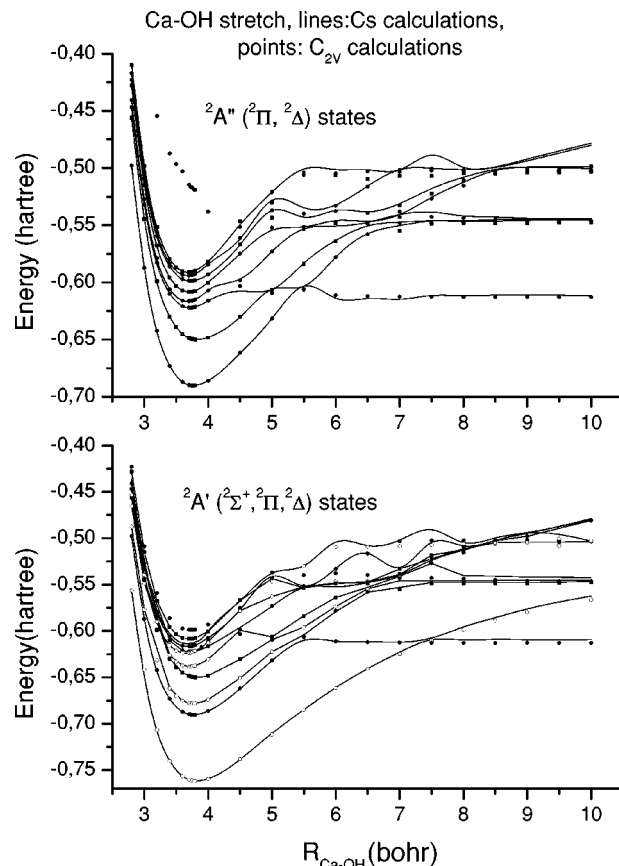
Ab initio MRD-CI calculations have been carried out on electronic states of CaOH for linear and bent geometries involving different values of the Ca-O bond length, varying from 2.8 bohr to 10.0 bohr, and of the bond angle between

FIG. 1. Ca-O stretching potentials obtained from C_{2v} calculations for O-H bond length=1.742 351 bohr.

110° and 180° . The O-H bond length was fixed for these calculations at the experimental value 0.922 Å.^{1,3} In an additional set of calculations in which the Ca-O bond length was varied between 3.5 and 3.9 bohr and the bond angle between 130° and 180° , the O-H bond length was changed from the above value to the bond length of OH^- [0.970 Å (Ref. 23)], in which intervals also lie other experimental¹⁰ as well as theoretical estimates¹²⁻¹⁴ of the O-H bond length in the ground electronic state of CaOH.

For the K and L shells of Ca and the K shell of O, effective core potentials have been employed.^{24,25} The valence AO basis sets employed for Ca and O are listed in Table I. The AO basis set for hydrogen is the $(6s/4s)$ ²⁶ augmented with $2p$ polarization functions (exponents 0.7 and 0.2) and s (exponent 0.025) and p (exponent 0.035) diffuse functions.

Before adopting the above basis sets, test calculations were carried out with different basis sets, with and without effective core potentials, including the AO basis set employed previously,¹¹⁻¹⁴ in order to examine the convergence of the results with the basis set. Furthermore, exploratory calculations for testing the CI procedure were carried out, involving 17, 9, and 7 electrons, respectively, in the CI calculations. It was found that for excitation energies, the results of the 7-electron configuration interaction calculations of the present work were comparable to those of previous work.¹⁵ As also found previously,¹¹ a larger value is obtained

FIG. 2. Linear Ca-O stretching potentials obtained from Cs calculations (solid lines) and C_{2v} calculations (points), for O-H bond length=1.742 351 bohr.

Ca-O stretch, <CaOH 160 deg and 120 deg

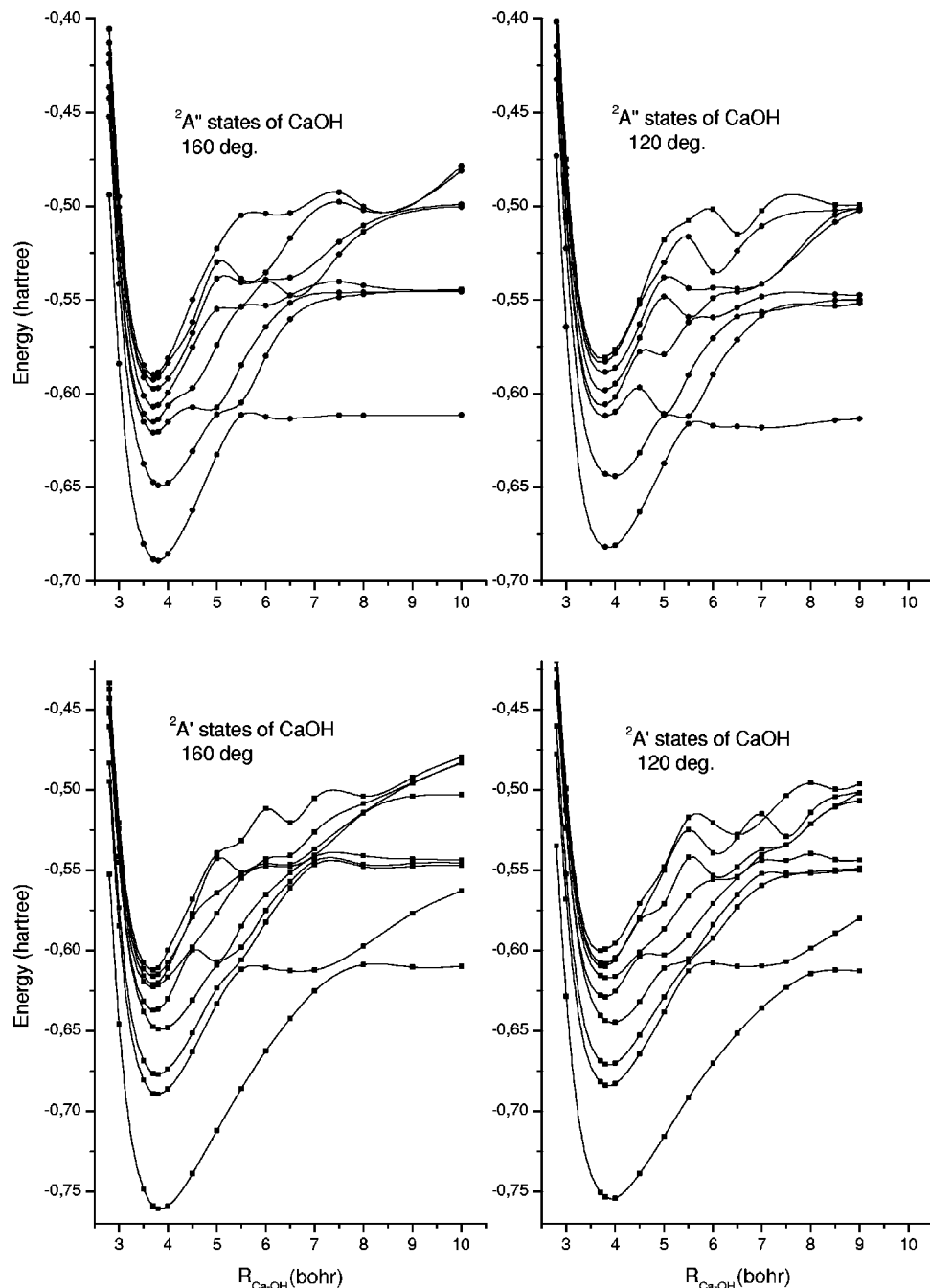


FIG. 3. Ca–O stretching potentials, for bond angles=160° and 120° and for O–H bond length=1.742 351 bohr.

for the ground state equilibrium Ca–O bond length with the 7-electron than with the 17-electron CI calculations, the latter being closer to the experimental value. The 9-electron calculations also overestimate the ground state equilibrium bond length. It has been found that the precise calculation of the Ca–O bond length in CaOH and in CaO requires the inclusion of core–electron correlation.²⁷ In the present work the main object is the determination of potential energy surfaces of a large number of excited states of CaOH rather than the precise determination of the molecular geometry. For this reason the 7-electron treatment has been employed in the present calculations, in order to keep the calculations tractable.

While most calculations have been carried out in C_s symmetry, which is the common point group symmetry for both bent and linear conformations, one series of calculations has been carried out in C_{2v} symmetry in order to identify the linear states. In the latter calculations the ${}^2\Sigma^+$ states are obtained as 2A_1 , the ${}^2\Pi$ states (and ${}^2\Phi$ at the dissociation limits, see below) are obtained as 2B_1 and 2B_2 , the ${}^2\Delta$ states as 2A_1 and 2A_2 and the ${}^2\Sigma^-$ as 2A_2 . In the C_s calculations the ${}^2\Sigma^+$ states are obtained as ${}^2A'$, the ${}^2\Sigma^-$ as ${}^2A''$ and the ${}^2\Pi$, (${}^2\Phi$) and ${}^2\Delta$ states as ${}^2A'$ and ${}^2A''$ pairs. Large reference sets for the generation of the configurations of the CI calculations have been employed, determined by preliminary calculations over the different geometries considered. At

TABLE II. Vertical transition energies (eV) of the electronic states of CaOH (Ca–O=3.8 bohr and O–H=1.742 351 bohr).

| C_{2v} States | C_{2v} ΔE_v | C_s states | C_s^a ΔE_v | Other theor. ^b | Expt. ^c states, ΔE |
|--------------------|--------------------------|-----------------|--------------------------|------------------------------|--|
| 1^2A_1 | 0.0 | $1^2A'$ | 0.0 | 0.0 | $\bar{X}^2\Sigma^+$, 0.0 |
| 1^2B_1 | 1.93 | $2^2A', 1^2A''$ | 1.93, 1.93 1.93, 1.94 | 1.880 | $\bar{A}^2\Pi$, 1.984 |
| 2^2A_1 | 2.26 | $3^2A'$ | 2.26, 2.26 | 2.226 | $\bar{B}^2\Sigma^+$, 2.234 |
| $3^2A_1, 1^2A_2$ | 3.04, 3.03 | $4^2A', 2^2A''$ | 3.05, 3.04 3.07, 3.05 | 3.021 | $\bar{C}^2\Delta$, 2.716 |
| 4^2A_1 | 3.35 | $5^2A'$ | 3.35, 3.36 | 3.285 | $\bar{D}^2\Sigma^+$, 3.490 |
| 5^2A_1 | 3.77 | $6^2A'$ | 3.78 | 3.702 | $\bar{E}^2\Sigma^+$, 3.704 |
| 2^2B_1 | 3.79 | $7^2A', 3^2A''$ | 3.80, 3.78 3.79, 3.78 | 3.721 | $\bar{F}^2\Pi$, 3.746 |
| 3^2B_1 | 3.95 | $8^2A', 4^2A''$ | 3.95, 3.95, 3.96, 3.96 | 3.875 | $\bar{G}^2\Pi$, 4.046 |
| 6^2A_1 | 4.03 | $9^2A'$ | 4.05, 4.05 | 3.946 | $H^2\Sigma^+$ |
| $7^2A_1, 2^2A_2$ | 4.19, 4.20 | $5^2A''$ | 4.17, 4.18 | 4.063 | $2^2\Delta$ |
| 8^2A_1 | 4.32 | | | | $6^2\Sigma^+$ |
| 4^2B_1 | 4.42 | $6^2A''$ | 4.42, 4.42 | | $4^2\Pi$ |
| 9^2A_1 | 4.51 | | | | $7^2\Sigma^+$ |
| 5^2B_1 | 4.56 | $7^2A''$ | 4.57 | | $5^2\Pi$ |
| 3^2A_2 | 4.64 | $8^2A''$ | 4.65 | | $3^2\Delta$ |
| 4^2A_2 | 6.65 | | | | |
| 5^2A_2 | 6.65 | | | | |
| 6^2A_2 | 7.84 | | | | |

^aUpper values $T=0.5 \mu\text{hartree}$, lower $T=0.025 \mu\text{hartree}$ ^bReference 15.^cReference 9.

short bond lengths the electronic states of CaOH are characterized by a small number of configurations involving single excitations of the unpaired electron from essentially Ca $4s$ (corresponding to the $\bar{X}^2\Sigma^+$ ground state of CaOH) to $4p, 3d$, etc., states. However at intermediate and large bond lengths the electronic states change character drastically and require configurations with three or more open shells. At the dissociation limits, the ground state is $\text{Ca}(4s^2^1S) + \text{OH}(X^2\Pi)$ leading to the $^2\Pi$ ground state for CaOH, whereas the next limit is $\text{Ca}(4s4p^3P^o) + \text{OH}(X^2\Pi)$ yielding $^2\Sigma^+$, $^2\Sigma^-$, $^2\Pi$, and $^2\Delta$ states (and spin quartets), and the next dissociation limit $\text{Ca}(4s3d^3D) + \text{OH}(X^2\Pi)$ yields $^2\Sigma^+$, $^2\Sigma^-$, $(2)^2\Pi$, $^2\Delta$, and $^2\Phi$ states. In the C_{2v} calculations nine states of 2A_1 symmetry, five of 2B_1 and six of 2A_2 symmetry have been calculated, employing 70, 61, and 58 reference configurations, respectively, with respect to which all single and double excitations are generated. Selection with a threshold (T) of $0.5 \mu\text{hartree}$ resulted in CI spaces varying between 50 000 and 100 000 configurations at the different geometries. In all the calculations presented in the present work, extrapolation of the calculated eigenvalues to $T=0$ was carried out as well as a full-CI correction.²⁸ In the C_s calculations, the reference spaces consisted of 71 configurations for the $^2A'$ and 75 configurations for the $^2A''$ calculations. The same selection threshold as in the C_{2v} calculations, $0.5 \mu\text{hartree}$, was employed for calculations involving values of the Ca–O bond length between 2.8 and 10.0 bohr and for the $\angle\text{CaOH}$ bond angle between 110° and 180° . The O–H bond length was fixed at the experimental r_0 value of 0.922 \AA or $1.742\ 351$ bohr. The CI spaces of these calculations varied between 100 000 and 200 000 configurations over the different geometries. Finally, calculations for short Ca–O bond lengths between 3.2 and 4.2 bohr, corresponding

to the region of the minima, and the same angle range as above, employed a selection threshold of $0.025 \mu\text{hartree}$, resulting in CI spaces of 300 000–400 000 configurations, in order to have more precise determinations in that region. In the latter set of calculations, for bond angles between 130° and 180° variations in the O–H bond length were also considered, taking values between 1.742 351 and 1.84 bohr (the latter value being slightly larger than the experimental equilibrium bond length of the OH radical) in order to obtain theoretical estimates of the equilibrium geometries of the different states. The experimental values for the O–H bond length in the ground state of CaOH vary from $0.901\text{--}0.922 \text{ \AA}$ ($1.703\text{--}1.743$ bohr) for r_0 (Refs. 1, 3, 4) and $0.930\text{--}0.9562 \text{ \AA}$ ($1.757\text{--}1.807$ bohr) for r_e .^{4,10} The variation in the experimental values for the Ca–O bond length in CaOH is smaller, $1.985\text{--}1.986 \text{ \AA}$ for r_0 (Refs. 1, 4, and 10) and $1.9746\text{--}1.976 \text{ \AA}$ for r_e .^{4,10}

RESULTS AND DISCUSSION

The Ca–O stretching potential energy curves obtained from the C_{2v} calculations are shown in Fig. 1(a) ($^2\Sigma^+$ states) and Fig. 1(b) ($^2\Pi$, $^2\Delta$, and $^2\Sigma^-$ states). As shown, the excited states have typical Rydberg minima for Ca–O distances between 3.65 and 3.8 bohr, but at larger distances they show interactions and avoided crossings, especially in the potentials of the $^2\Pi$ states. The Ca–O stretching potential energy curves obtained from the calculations in C_s symmetry appear to be even more complicated, cf. Fig. 2. However the seemingly spurious bumps can be resolved at linear geometries in terms of crossings between different states having the same symmetry in the C_s point group, as shown in Fig. 2, where the lines are obtained from the C_s and the points from the

Bending potentials at Ca-O 3.8 bohr and O-H 1.742351 bohr

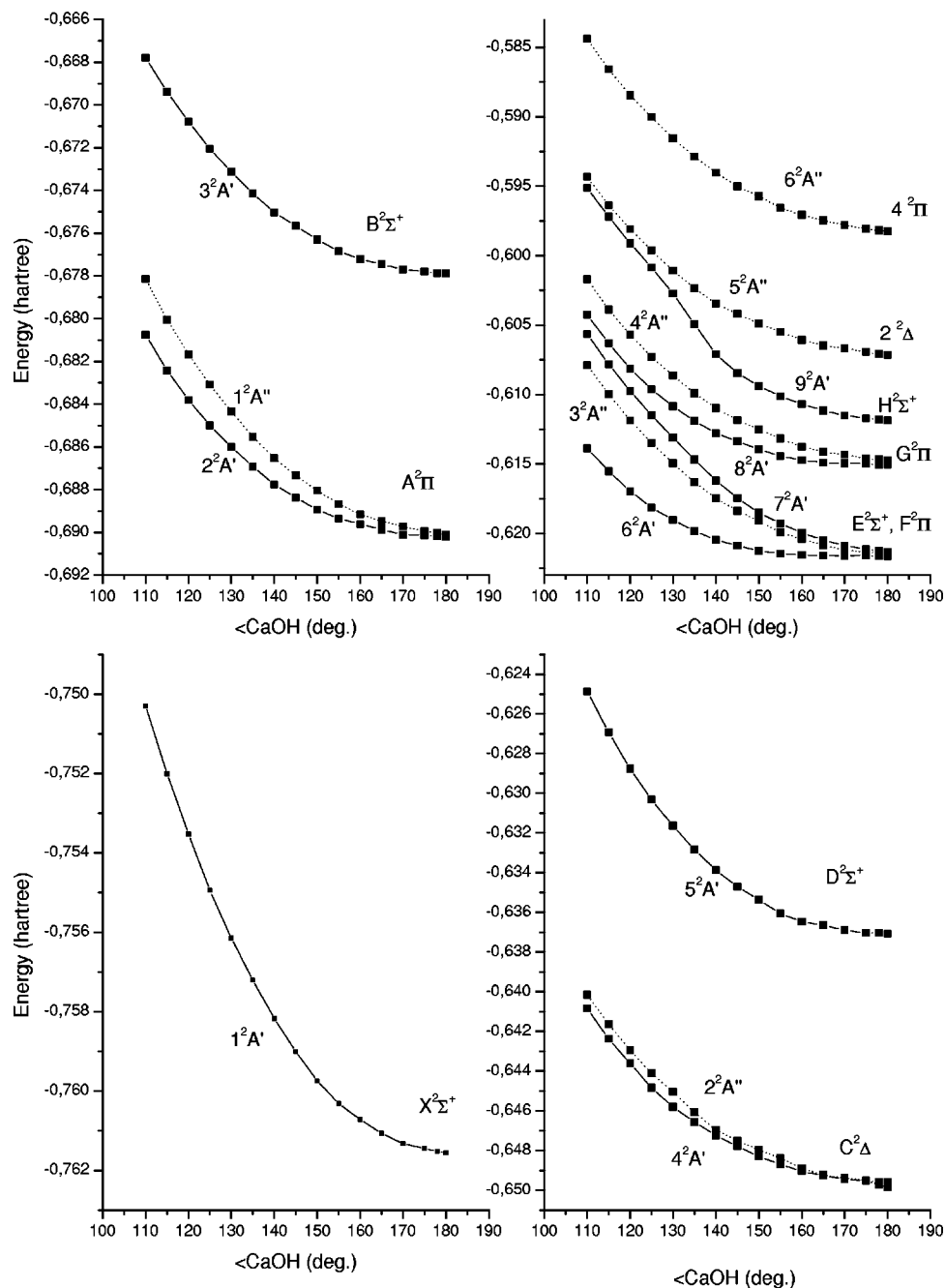


FIG. 4. Bending potentials for Ca-O bond length=3.8 bohr and O-H bond length=1.742 351 bohr.

C_{2V} calculations. For nonlinear geometries, the Ca-O stretching potentials retain their basic appearance, with small variations in the barrier heights, cf. Fig. 3, where typical Ca-O stretching potentials have been plotted for bond angles of 160° and 120° . It may be seen in Fig. 3 that, as also mentioned above, for Ca-O bond lengths smaller than about 4.5 bohr, the potential energy curves of the excited states of CaOH have the typical appearance of Rydberg states, while at larger bond lengths they become very complicated. The same type of qualitative picture has also been obtained previously for the potential energy curves of the excited states of MgOH and BeOH.¹⁷

Transition energies from the ground to excited electronic

states of CaOH, up to $\tilde{H}^2\Sigma^+$, including experimental T_0 values and theoretical vertical energies at the optimized geometry of 2.019 Å for Ca-O and 0.967 Å for O-H of ground state CaOH have been compiled by Hailey *et al.*⁹ Those values are compared to the transition energies of the present work calculated at Ca-O=3.8 bohr and O-H=1.742 351 bohr in Table II, where the results of the C_{2V} calculations as well as those for two sets of C_s calculations obtained with the $T=0.5$ and $T=0.025$ μ hartree calculations, respectively, are given. As shown in Table II, the C_{2V} and the C_s values are nearly identical. The agreement with the previous theoretical values is fair, as also with experimental values. For

Bending potentials for different Ca-O bond lengths

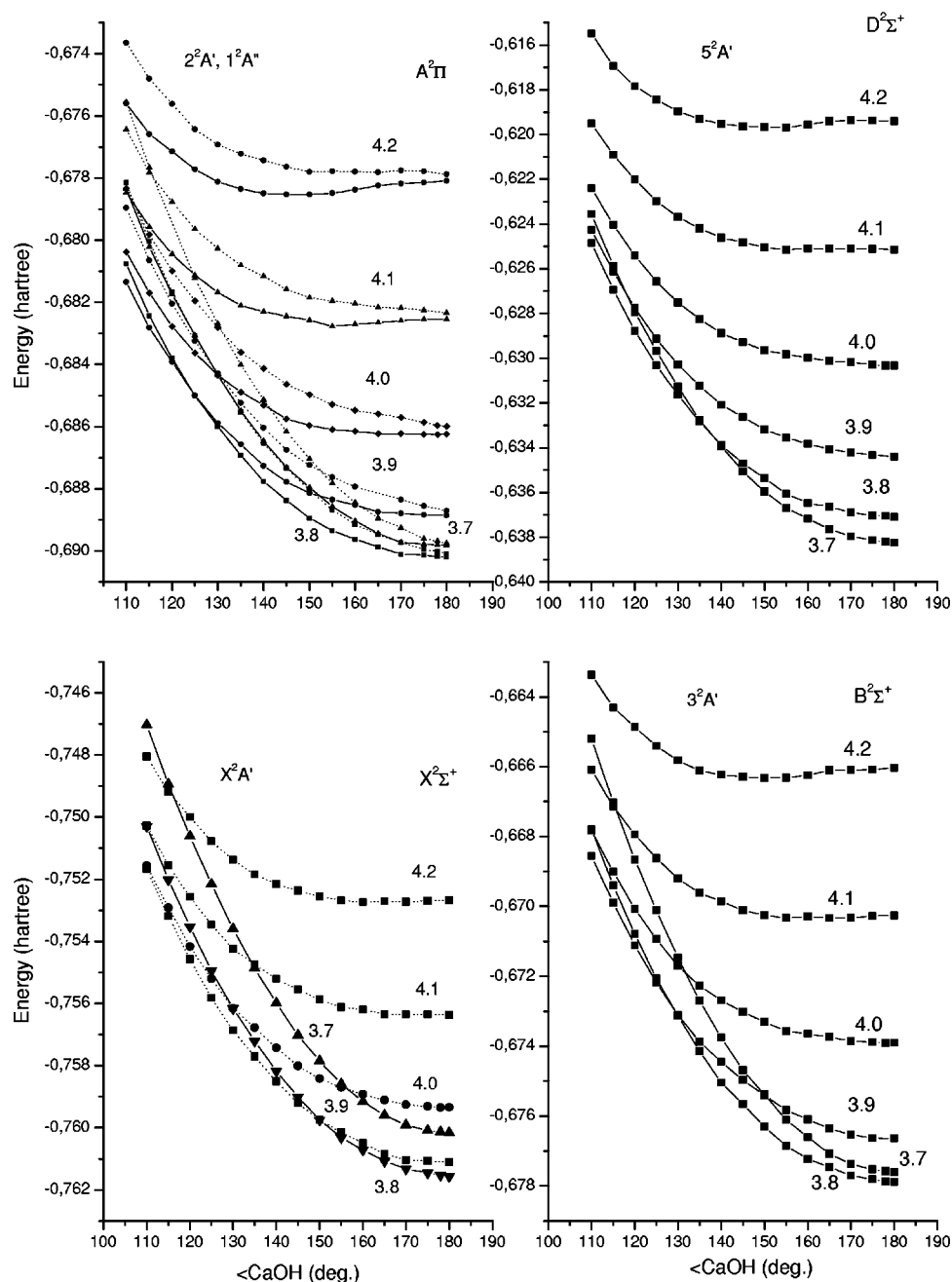


FIG. 5. Bending potentials for the X^2A' , $2^2A'$, and $1^2A''$, $3^2A'$, and $5^2A'$ states at different values of the Ca-O bond length and O-H bond length=1.742 351 bohr.

most of the transitions the theoretical values are within 0.05 eV (and within 0.1 eV for the higher states) of the experimental. However there is a large discrepancy (of about 0.33 eV) between the present theoretical and experimental T_0 values for the $\tilde{C}^2\Delta$ state, for which a similar difference is also found between the experimental and the theoretical values of previous work.¹⁵ Since the theoretical methods and basis sets employed in the present work are quite different from those of the previous theoretical study,¹⁵ and yet the calculated T_0 values for the $\tilde{C}^2\Delta$ state are within 0.03 eV of each other, it would seem that the experimental position of the $\tilde{C}^2\Delta$ state might be in error.

The calculated bending potentials for the various electronic states of CaOH, with the O-H bond length fixed at the r_0 value of 1.742 351 bohr and Ca-O bond length varying from 2.8–3.9 bohr, obtained at $T=0.5 \mu\text{hartree}$, all have their minima at 180° . A typical plot of the bending potentials is shown for a Ca-O bond length of 3.8 bohr and O-H = 1.742 351 bohr (0.922 Å) in Fig. 4. Allowing for the different vertical scale in these diagrams it may be seen that the bending potentials of the excited states generally resemble that of the ground state, with the exception of $6^2A'$ which is shallower. In fact, the $6^2A'$ state appears to be quasilinear in the sense that the bending potential is very flat near the linear

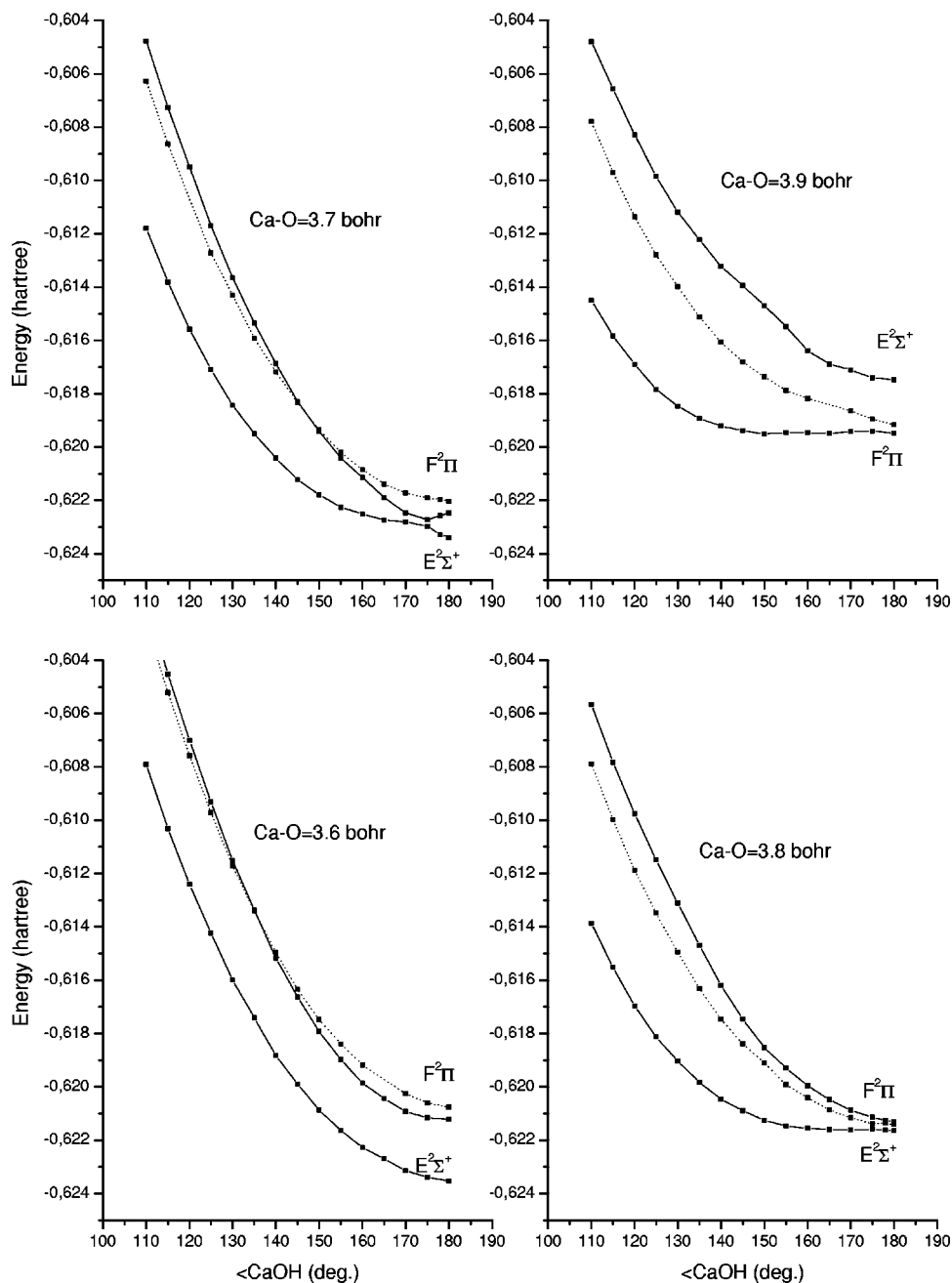
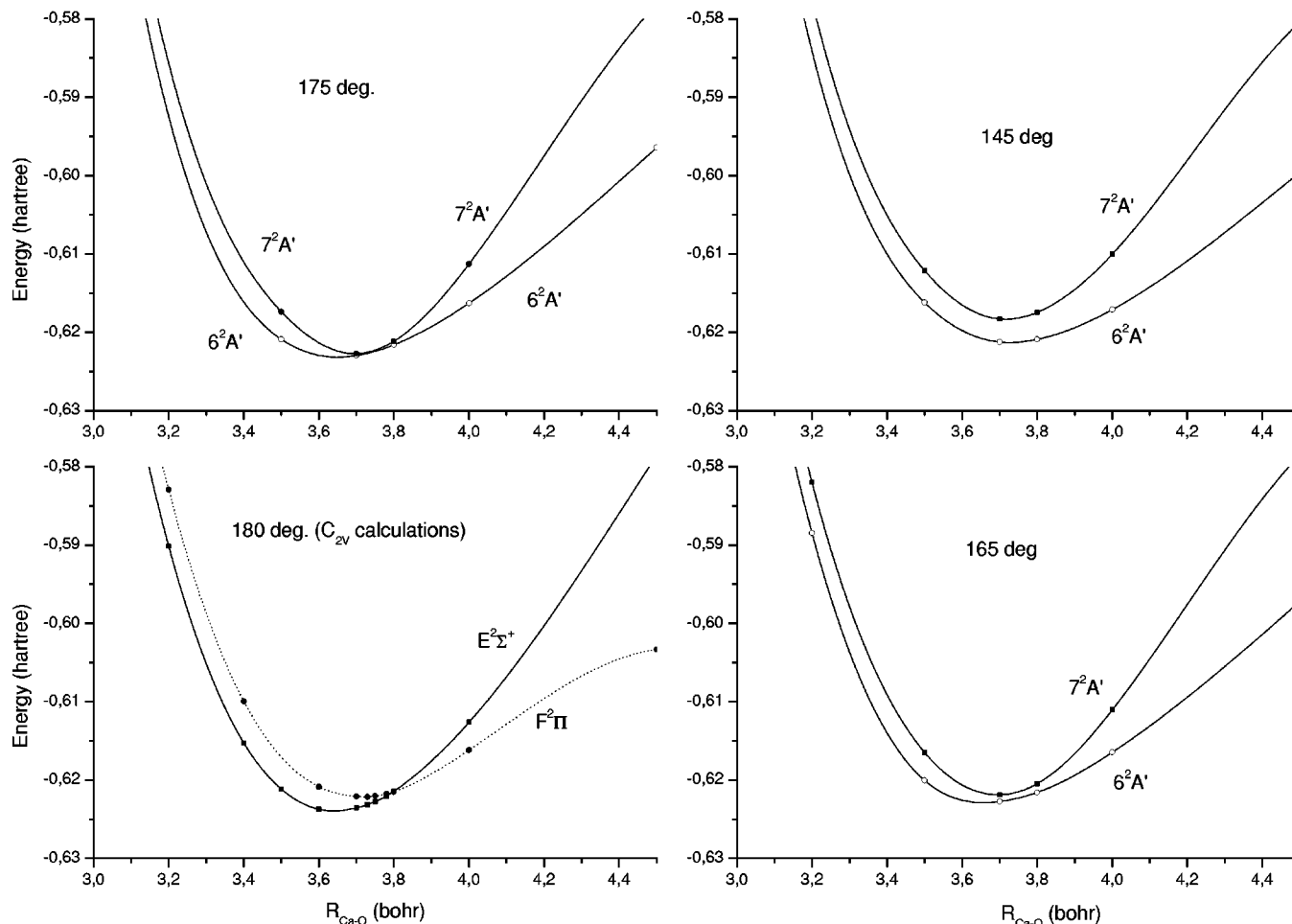
Bending potentials of $6^2A'$, $7^2A'$ and $3^2A''$ 

FIG. 6. Bending potentials of the $6^2A'$, $7^2A'$, and $3^2A''$, correlating with $\tilde{E}^2\Sigma^+$ and $\tilde{F}^2\Pi$, for different values of the Ca-O bond length and for O-H bond length=1.742 351 bohr.

geometry. Decreasing the bond angle from 180° down to 160° only raises the energy by 20 cm^{-1} , in the calculations shown in Fig. 4. At larger Ca-O bond lengths, bent geometries are favored, cf. Fig. 5, where bending potentials of the ground, $\tilde{A}^2\Pi$, $\tilde{B}^2\Sigma^+$, and $\tilde{D}^2\Sigma^+$ states are shown for different values of the Ca-O bond length and with O-H fixed at 1.742 351 bohr. However at these geometries the calculated energies are much higher than for the shorter bond lengths (cf. Fig. 6). Thus in the potential energy curves presented thus far there is no evidence for a bent $\tilde{F}^2\Pi$ excited state of CaOH, which correlates with a linear $^2\Pi$ state, as has been proposed previously on the basis of the observed spectra. The state most closely resembling this description would

be the $7^2A'$ state, which has a rather shallow minimum (with a barrier to linearity of about 50 cm^{-1} along this cross section) in the bending potential for Ca-O=3.7 bohr, at 175° , which results from an avoided crossing between the $6^2A'$ and $7^2A'$ states (cf. Fig. 6). This might be contrasted with the MgOH and BeOH systems, where as mentioned in the Introduction, our calculations have shown that the first excited state in both systems is bent, with relatively deep minima, of 2216 cm^{-1} at a bond angle of 115° and 3710 cm^{-1} at 116° , respectively.¹⁷

It should be also noted that the order of the adiabatic $^2A'$ states correlating with the $\tilde{E}^2\Sigma^+$ and the $\tilde{F}^2\Pi$ varies with Ca-O bond length. For Ca-O greater than 3.8 bohr $6^2A'$

$6^2A'$ - $7^2A'$ interaction with Ca-O stretchingFIG. 7. Details of the stretching potentials of the $6^2A'$, $7^2A'$ states at different values of the bond angle.

$+3^2A''$ correlate with $\tilde{F}^2\Pi$ and $7^2A'$ with $\tilde{E}^2\Sigma^+$ while for shorter bond lengths (e.g., 3.6 bohr), $7^2A'+3^2A''$ correlate with $\tilde{F}^2\Pi$ and $6^2A'$ with $\tilde{E}^2\Sigma^+$, cf. Fig. 6. At a Ca–O bond length of 3.7–3.8 bohr and a bond angle of 180° all three states, $6^2A'$, $7^2A'$, and $3^2A''$, lie close in energy. Although it appears that it is $7^2A'$ that correlates with $\tilde{F}^2\Pi$, this is only the case at bond angles very near 180° , while there is the above mentioned avoided crossing between the $6^2A'$ and $7^2A'$ states at a bond angle of 175° , cf. Fig. 6. It is instructive to compare the Ca–O stretching potentials of the $6^2A'$ and $7^2A'$ states at different bond angles, including the linear calculations, shown in Fig. 7. As shown there, at the linear geometries there is a crossing of the $\tilde{E}^2\Sigma^+$ and $\tilde{F}^2\Pi$ states at a Ca–O bond length of 3.75 bohr. When the bond angle decreases, the basic structure is retained except that now the crossing becomes avoided crossing and the curves move apart for smaller bond angles (cf. plot at 145° in Fig. 7). The present findings are in agreement with the experimental evidence of mixing between the \tilde{E} and \tilde{F} states,⁸ for which there is only a difference of 336 cm^{-1} between the T_0 values assigned to the $\tilde{E}\rightarrow\tilde{X}$ and $\tilde{F}\rightarrow\tilde{X}$ transitions.

As mentioned in the preceding sections, larger CI calcu-

lations (employing a threshold of $0.025\ \mu\text{hartree}$) have been carried out for the region of the geometries with Ca–O bond length between 3.2 and 4.2 bohr, which includes the Rydberg minima of the stretching potentials (cf. Fig. 1). Furthermore, variations in the O–H bond length were considered, since there is a wide difference between the reported experimental values for the O–H bond length in CaOH. There is no significant difference between the results of the smaller CI and those of the larger CI calculations, with O–H fixed at 1.742 351 bohr. When the O–H bond length is varied, larger values are favored for the ground as well as the excited states, as will be discussed below. In Table III, the linear geometries corresponding to minima in the calculated energies are given. As shown in Table III, most states favor a value near 1.80 bohr for the O–H bond length, which is close to the experimental r_e value of Li and Coxon for the ground and the $\tilde{A}^2\Pi$ state, 1.806 98 and 1.808 870 bohr, respectively.¹⁰ However, the present calculations overestimate the Ca–O bond length by about 0.1 bohr, compared with the experimental r_e values of 3.732 and 3.691 06 bohr for the above two states, respectively.¹⁰ The trend of decreasing Ca–O bond length in going from the ground state to

TABLE III. Minimum energy linear geometries and transition energies of the electronic states of CaOH.

| States | CaOH=180° $R_{\text{Ca-O}}$ (bohr), $R_{\text{O-H}}$ (bohr) | T_e (eV) |
|--|--|---------------|
| \bar{X}^2A' ($\bar{X}^2\Sigma^+$) | 3.83, 1.80 | 0.0 |
| $2^2A'$, $1^2A''$ ($\bar{A}^2\Pi$) | 3.76, 1.80 | 1.94, 1.95 |
| $3^2A'$ ($\bar{B}^2\Sigma^+$) | 3.77, 1.80 | 2.28 |
| $4^2A'$, $2^2A''^a$ ($\bar{C}^2\Delta$) | 3.83, 1.80 | 3.06, 3.05 |
| $5^2A'$ ($\bar{D}^2\Sigma^+$) | 3.70, 1.80 | 3.37 |
| $6^2A'$ ($\bar{E}^2\Sigma^+$) | 3.65, 1.82 | 3.74 |
| $7^2A'$, $3^2A''$ ($\bar{F}^2\Pi$) | 3.70, 1.80 | 3.80, 3.79 |
| $8^2A'$, $4^2A''$ ($\bar{G}^2\Pi$) | 3.68, 1.80 | 3.96, 3.95 |
| $9^2A'$ ($\bar{H}^2\Sigma^+$) | 3.68, 1.81 | 4.04 |
| $5^2A''$ ($2^2\Delta$) | 3.68, 1.81 | 4.18 |
| $6^2A''$ ($4^2\Pi$) | 3.72, 1.80 | 4.43 |
| $7^2A''$ ($5^2\Pi$) | 3.68, 1.80 | 4.56 |
| $8^2A''$ ($3^2\Delta$) | 3.68, 1.81 | 4.64 |

^aBent minimum of $2^2A''$ at 170°, Ca–O=3.83 bohr, O–H=1.80 bohr, with barrier to linearity of 84 cm⁻¹.

^bBent minimum at 175°, Ca–O=3.7 bohr, O–H=1.79 bohr, with a barrier to linearity of 92 cm⁻¹.

$\bar{A}^2\Pi$ is well reproduced (cf. Table III), however, and similarly for the equilibrium bond length of the $\bar{D}^2\Sigma^+$ state, for which the experimental estimate for the equilibrium Ca–O bond length is 1.894 Å (3.579 bohr).⁸ As shown in Table III, all the excited states calculated have shorter Ca–O bond lengths than the ground state, with the exception of $4^2A'$ and $2^2A''$ states which correlate with $\bar{C}^2\Delta$, and have the same equilibrium linear geometry as the ground state. Again, there is no evidence for a bent state with a considerable minimum, while the $7^2A'$ state correlating with $\bar{F}^2\Pi$ has a minimum at Ca–O=3.70 bohr, O–H=1.79 bohr and a bond angle of 175°, with a barrier to linearity of 92 cm⁻¹. Similarly, the $2^2A''$ state correlating with the $\bar{C}^2\Delta$ state has a shallow minimum of 84 cm⁻¹ at 175° and Ca–O=3.81 bohr and O–H=1.80 bohr. While the magnitude of these well-depths is well within the expected errors in the present calculations, their persistence when the CI calculation is enlarged is indicative that these minima do exist. Furthermore, similar calculations on the ground state of BeOH obtained a minimum of 50 cm⁻¹, in close agreement with the results (45–60 cm⁻¹) of other calculations employing methods, not involving selection of configurations.¹⁷

It might be noted that the calculated minima for the $2^2A'$ states are rather broad in the sense that a number of different geometries around the linear minimum, corresponding to small variations in the Ca–O bond length, the O–H bond length and the bond angle, have very similar energies. Slightly lower minima (by 5–15 cm⁻¹) are found for a bond angle of 175° than for the linear geometries in the cases of $2^2A'$, $4^2A'$, and $6^2A'$ states and also for the ground state. By contrast, all the $2^2A''$ calculated, with the exception of $2^2A''$ (see above), have linear minimum energy geometries. It is rather tenuous to insist on the existence of the above off-linear minima found for some of the $2^2A'$ states, given the small energy differences involved and the accuracy of the present calculations. However, the present results indicate

that, as mentioned above, for certain of the electronic states of CaOH a number of molecular geometries involving small variations in the molecular parameters, including the bond angle, have nearly identical energies. Much larger calculations, including core correlation effects might yield a more precise determination of the equilibrium geometries of the ground and excited states of CaOH. Recent RCCSD(T) calculations on the ground state of CaOH, employing quadruple-zeta and quintuple-zeta basis sets and 17-electrons in the CI calculations resulted in excellent agreement of theoretical and experimental bond lengths as well as vibrational-rotational term values and B_v values.²⁷ As shown in Table III, the calculated transition energies corresponding to the minimum energy geometries (T_e) are not significantly different from the vertical transition energies listed in Table I, demonstrating that there is a nearly uniform lowering of the energies of the states calculated when the O–H bond length is increased from 1.742 351 to 1.80 bohr.

CONCLUSIONS

Effective-core MRDCI calculations have been carried out on the potential energy surfaces of the ground and excited electronic states of CaOH. The calculated transition energies are in good agreement with previous theoretical and with experimental values, with the exception of the $\bar{C}^2\Delta \rightarrow \bar{X}^2\Sigma^+$ transition energy for which there is a discrepancy between the theoretical and the experimental values of over 0.33 eV. All the states calculated favor linear geometries, with the exception of $2^2A''$ state (correlating with $\bar{C}^2\Delta$) and $7^2A'$ (correlating with $\bar{F}^2\Pi$). These states are quasilinear with a barrier to linearity of 84 cm⁻¹ and 92 cm⁻¹, respectively.

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